Transesterification of canola oil to biodiesel using calcium bentonite functionalized with K compounds

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ABSTRACT

The transesterification reaction of canola oil and methanol to biodiesel was investigated using a calcium bentonite based catalyst support that was functionalized with KF, KOH and K_2CO_3. Transesterification reaction time, methanol to oil molar ratio, temperature and catalyst loading level were the principal parameters. The activity of KF impregnated catalyst was superior to those of KOH and K_2CO_3 catalysts. Methyl ester yields which were as high as $98.2 \pm 1.4\%$ could be obtained with KF impregnation.

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1. Introduction

Production of biodiesel has become an important issue due to the increases in energy demand and cost, environmental considerations and reductions in fossil fuel reserves. A potential diesel fuel substitute is biodiesel, i.e., methyl esters of fatty acids (FAME), that can be produced by the transesterification reaction of triglycerides of vegetable oils with short-chain alcohols, mainly methanol. Compared to fossil-based diesel fuels, biodiesel processes have many advantages. For example, biodiesels are obtained from renewable resources and are biodegradable. Biodiesels also generate cleaner engine emissions, and offer superior lubrication [1].

The industrial synthesis reactions for biodiesel have generally been carried out over basic catalysts such as sodium or potassium hydroxide, methoxide, or carbonate, which were shown to generate relatively high reaction rates [2]. Enzyme based transesterification is also possible but the high price and instability of enzymes render the commercialization of enzyme-catalyzed systems prohibitive [3,4]. Homogeneous catalysts can be used for industrial synthesis and furnish relatively short reaction times (such as <1 h). However, homogeneous catalysts cannot be readily removed from biodiesel products and the necessary treatments of the resulting alkaline

and acidic wastewaters increase the operating costs. The use of solid catalysts, instead of homogeneous liquid catalysts, reduces the cost of biodiesel synthesis [2,5]. Heterogeneous solid catalysts are also frequently used and offer the advantages of being amenable to relatively easy separation from the biodiesel product and the higher quality of their ester products and glycerol by-products. An additional benefit of heterogeneous solid based catalysts is their relatively low consumption in comparison to that of homogeneous systems [6–8].

Earlier studies of heterogeneously catalyzed transesterification reactions of vegetable oils have focused on the use of basic single-metal oxides including calcium oxide [9–13], magnesium oxide [14] and strontium oxide [15]. Mixed metal oxides were also applied in order to enhance the basicity of the catalysts during the transesterification reaction. Al_2O_3-SnO and Al_2O_3-ZnO [16], Mg-La oxides [17], $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$, and $CaCeO_3$ catalysts [18] exhibited the highest base strengths and gave rise to methyl ester yields which varied between 80% and 99%.

Previous studies have shown that heterogeneous catalysts functionalized with sodium and potassium compounds are promising for the synthesis of biodiesel from vegetable oils. The catalytic activity of supported potassium compounds principally depends on the type of the carrier, the potassium loading and the conditions of pretreatment. Alumina [19–23], nano alumina [24], calcium oxide [9,10,13], magnesium oxide [25–27], zinc oxide [19,28], zeolite [29], silica [30] and dolomite [31] were modified with sodium and potassium compounds and were used as effective catalyst support materials.

Research on the use of clays such as zeolite, dolomite, kaolin and bentonite as catalysts or catalyst supports has attracted attention in recent years [29,31–33]. However, there is only one report available on the use of bentonite as a catalyst support for transesterification [33] in spite of its industrial importance. Soetaredjo et al., used a KOH/bentonite catalyst for the transesterification of palm oil to biodiesel and obtained a maximum yield of $90.7 \pm 2.7\%$ under the reaction conditions of 6:1 methanol to oil ratio, 3 wt.% catalysts at $60\,^{\circ}C$ in 3 h [33].

Bentonite is a natural clay (Al, $Fe_{0.67}$ $Mg_{0.33}$) $Si_4O_{10}(OH)_2Na,Ca_{0.33}$) results from the weathering of volcanic ash in the presence of water. Different types of bentonite are differentiated from each other on the basis of the element that is dominant in its composition, i.e., typically K, Na, Ca, and Al. Calcium bentonite is the generally-preferred bentonite on the basis of its lower cost, environmental friendliness, stability and reusability and is widely used in pelletizing applications, fertilizers, seed coatings and effluent treatment [34].

In the present work, a number of calcium bentonite-based heterogeneous catalysts were prepared and used in the methanol synthesis of biodiesel from canola oil using a liquid batch reactor. The catalysts utilized three different K compounds (KF, KOH, K_2CO_3) which were loaded to calcium bentonite at different loading ratios. The catalysts were characterized using XRD, SEM-EDS and N_2 adsorption-desorption for BET surface area. The Hammett indicator procedure was applied in order to determine the basicity of the synthesized catalysts [19,35,36]. The methyl ester yields were determined as a function of reaction conditions and the type and concentration of the K compound used for the functionalization of the surfaces of calcium bentonite.

2. Experimental

2.1. Materials

The calcium based bentonite used in the present work was obtained from Eskisehir region of Turkey. The water absorbance of the as-received calcium bentonite was determined to be 0.8 ± 0.02 g per g of bentonite. KF and KOH (analytical-grade with a purity of 99.8 vol.%) were obtained from Merck. K_2CO_3 and analytical-grade methanol were supplied by Riedel-de Haën. The canola oil was purchased from a local food market. The free fatty acid content of the canola oil was determined to be 0.085 wt.% following the AOCS Official Method Cd 3a-63 procedure [37].

2.2. Catalyst synthesis

Calcium bentonite was crushed and granulated using a mortar and a pestle. The resulting bentonite was dried and sieved. The particles which were collected on 45 and 60 mesh sieves were used as the catalyst supports. Aqueous solutions of the K compounds (KF, KOH and K_2CO_3) were prepared. Care was exercised during the preparation of the KF solution since KF is poisonous by inhalation and ingestion (lethal at the g level) and is highly corrosive, i.e., skin contact may cause severe burns. The calcium bentonite particles were impregnated with the aqueous solutions of the K compounds. The aqueous K solution was pumped drop wise using a peristaltic pump and was absorbed by the calcium bentonite particles.

The catalyst support samples will be referred to on the basis of the weight percentage of the K compound in bentonite. Thus, 40 weight percent of KF (40 wt.% KF) will indicate the weight of KF over the dry weight of bentonite particles functionalized with KF. The typical procedure for the impregnation of the (40 wt.% KF) sample involved the placement of 3 g of calcium bentonite into a 250 ml flask held in an ultrasonic water bath and the drop-wise pumping of

KF solution containing 2 g of KF dissolved in 2.4 g of deionized water (therefore 40% by weight of KF in KF-functionalized bentonite). The KF-functionalized calcium bentonite samples were prepared at 10, 20, 30 and 40 wt.% KF. The same procedure was used for the preparation of bentonite samples upon impregnation of 40% by weight of KOH and K_2CO_3 in functionalized bentonite.

Calcium bentonite particles, impregnated with KF, KOH and K_2CO_3, were dried in a vacuum oven at 393 K for 16 h. Upon drying, the calcium bentonite particles were calcined at 773 K for 3 h.
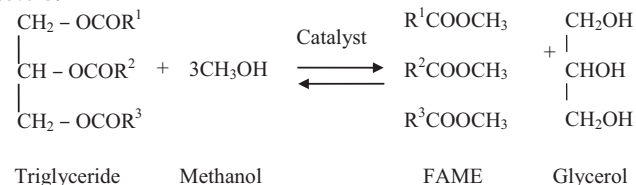
2.3. Catalyst characterization

The BET surface area values of the catalyst particles were characterized via a nitrogen absorbance method using a multipoint BET sorptometer. Prior to each surface area measurement, all samples were kept in an oven overnight under vacuum at 383 K.

The characterizations of the basic strength and basicity of the synthesized catalysts were performed by a Hammett indicator procedure, outlined in detail by Xie et al. [19,35,36] and Boz et al. [22,24]. This procedure involves placing about 300 mg of the sample into a one ml solution of Hammett indicators followed by dilution with 10 ml of methanol. Two hours were allowed to elapse for equilibrium to be reached, as indicated by color stability. The basic strength is defined as being stronger than the weakest indicator, which exhibits a color change, however weaker than the strongest indicator that produces no color change. The Hammett indicators were bromothymol blue ($H_- = 7.2$), phenolphthalein ($H_- = 9.8$), 2,4-dinitroaniline ($H_- = 15.0$) and 4-nitroaniline ($H_- = 18.4$). The basicity values (mmol/g) of the samples were determined by the method of Hammett involving a benzene carboxylic acid indicator (0.02 mol/l anhydrous ethanol solution) and titration until the color changed back to the original color [19,35,36].

Intermediate compounds in the synthesized catalyst systems were analyzed by X-ray diffractometer using a Rigaku/D/MAX 2200 diffractometer. CuK_α radiation from a Cu X-ray tube running at 40 kV/40 mA at room temperature was used. The Bragg angle range was between 5 and 75°. SEM micrographs of the KF-loaded calcium bentonite catalyst particles were obtained using a Jeol JSM 6400 scanning electron microscope. The elemental chemical analysis of the synthesized catalyst surfaces was carried out using the energy dispersive X-ray spectroscopy (EDS) technique. The elemental analyses of calcium bentonite and functionalized calcium bentonite catalysts were carried out before and after the transesterification reaction.

2.4. Transesterification reaction of vegetable oil to biodiesel

The conversion of the vegetable oil to biodiesel, i.e., the transesterification reaction of triglycerides to fatty acid methyl esters:

$$
\begin{array}{ccccc}
CH_2 - OCOR^1 & & & R^1COOCH_3 & CH_2OH \\
| & & & & | \\
CH - OCOR^2 & + & 3CH_3OH \xrightarrow{\text{Catalyst}} & R^2COOCH_3 & + \; CHOH \\
| & & & & | \\
CH_2 - OCOR^3 & & & R^3COOCH_3 & CH_2OH \\
\end{array}
$$

Triglyceride   Methanol   FAME   Glycerol

was performed in a jacketed 250 mL batch reactor equipped with a reflux condenser and a magnetic stirrer. The reactor was initially filled with 50 g of canola oil, which was heated to the reaction temperature while stirring at 600 rpm. The effects of the catalyst type, the reaction temperature (298, 318, 333 and 338 K), molar ratio of methanol to oil (6:1-18:1), catalyst/oil weight ratio (1–7 wt.%), and the reaction time on the conversion ratio of the triglycerides to FAME were investigated. All of the experiments were performed under atmospheric pressure. The typical
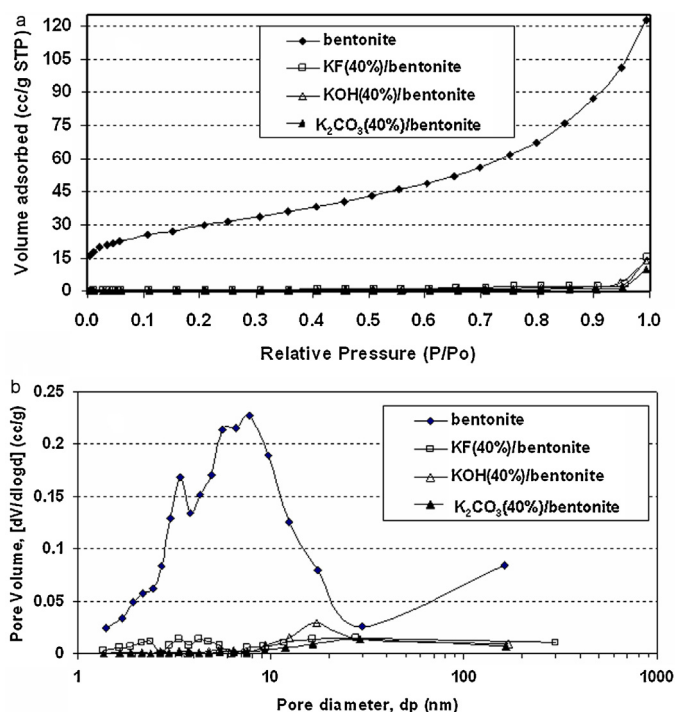
Fig. 1. (a) Nitrogen adsorption isotherms and (b) pore size distributions of calcium bentonite and calcium bentonite catalysts impregnated with different potassium compounds (KF, K_2CO_3, and KOH) prior to transesterification reaction.
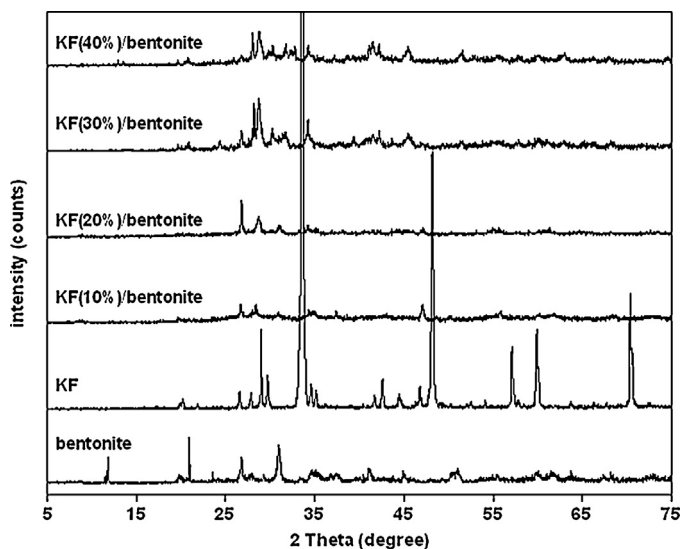
Fig. 2. XRD patterns of calcium bentonite, KF and calcium bentonite catalysts impregnated at different potassium fluoride loading levels (10–40 wt.%) upon calcination and prior to transesterification.

experiment involved the collection of about 2-3 ml of sample from the reactor sampling outlet at hourly intervals. The rate of conversion was determined not to be affected by the rotational speed of the stirrer in the 400–1000 rpm range and the rotational speed was kept constant at 600 rpm during all reaction runs.

After the transesterification reaction the products were separated by decantation within 24 h. The biodiesel and glycerol layers exhibit different densities of 0.86 and 1.126 g/cm³, respectively and thus could easily be separated from each other.

The methyl ester content of the decanted transesterification product was analyzed by an Agilent 6890 gas chromatograph equipped with a flame ionization detector and a CARBOWAX 20M capillary column. Sample preparation and GC analysis were carried out following European Standard of EN 14103 [38]. All data points were reproduced in triplicate and 95% confidence intervals, determined according to Student's-*t* distribution, are reported.

3. Results and discussion

3.1. Catalyst characterization

Physical properties and catalytic activities of the K functionalized catalysts are summarized in Table 1. The BET surface area of pure calcium bentonite was 104.8 m²/g. Upon impregnation with the K compounds there was a significant reduction of the surface area, i.e., the surface and pores of the catalyst support were covered upon impregnation. The surface areas of KF-doped catalyst particles decreased with increasing KF loading (Table 1). Nitrogen adsorption isotherms obtained with calcium bentonite and calcium bentonite catalysts impregnated with different potassium compounds (KF, K_2CO_3, and KOH), following calcination at 773 K for 3 h, are shown in Fig. 1a. The BET surface areas of different potassium compounds (KF, K_2CO_3, and KOH) were similar.

The nitrogen adsorption isotherms of calcium bentonite show the typical Type II isotherm. On the other hand, the nitrogen

adsorption isotherms of the synthesized catalysts exhibit the typical Type III isotherm, to indicate that the KF impregnated bentonite catalyst supports are macroporous and exhibit a low energy of adsorption [39]. Differential pore size distributions of the materials used in this study are illustrated in Fig. 1b. It can be understood that, the pore size distribution is quite narrow. Granados et al. have reported that the dimensions of methyl oleate (oleic acid methyl ester) and glycerin are around 2.5 nm and 0.6 nm, respectively [9]. The comparison of the mean pore size diameter of synthesized catalyst with the volume that would be occupied by triglyceride suggests that the triglyceride molecules can easily penetrate into the pores of the synthesized catalyst. Since most of the pores of the synthesized catalysts are in the 2–30 nm range most of the active sites would be utilized during the transesterification reaction.

The XRD patterns of calcium bentonite and catalysts with different KF loadings (10–40 wt.%) are shown in Fig. 2. The X-ray diffraction patterns of calcium bentonite particles exhibit primarily the dioctahedral smectite phase ($2\theta = 21, 26–28°, 29–30°, 35°$) and contain quartz ($2\theta = 26–27°$), feldspar ($2\theta = 11–12°, 28°$), calcite ($2\theta = 29–30°$) and opal crystobalite-tridymite ($2\theta = 23–24°$). Upon KF impregnation, the typical KF peaks were observed at the Bragg angles, $2\theta = 20.0°, 29.0°, 33.0°, 48.0°, 56.0°, 60.0°$ and $71.0°$. An additional K_2O phase appeared clearly in the diffraction patterns upon KF loading and calcination. The peaks associated with the K_2O phase are observed at $2\theta = 30.0°, 42.7$ and $53.0°$. The intensities of these peaks increased with increasing KF content.

Fig. 3 shows the typical SEM micrographs of calcium bentonite and KF(40%)/bentonite catalyst particles prior to and after the completion of the transesterification reaction. Fresh crystalline morphologies form at the surfaces of the functionalized catalyst after the impregnation with the aqueous KF solution and calcination (Fig. 3b). Reductions in the particle sizes of the catalyst particles occurred as a consequence of the granulation of the catalyst particles during agitation while the transesterification reaction is taking place (Fig. 3c).

3.2. Transesterification reaction

Table 1 reports the conversion of triglycerides to biodiesel in 7 h at 338 K, 3 wt.% catalyst loading and 6:1 molar ratio of methanol to canola oil for KF at four concentrations and KOH and K_2CO_3 at 40% by weight. The conversion achieved with KF is higher than

Table 1
Physical properties of calcium bentonite and K-functionalized calcium bentonite catalyst supports and methyl ester yields under similar transesterification conditions.[a]

|		BET area (m^2/g)	Basic strength (H_-)	Basicity (mmol/g)	Yield of Biodiesel (%)
1	Calcium bentonite	104.8	<7.2	0.15 ± 0.05	5.9 ± 1.2
2	KF(10%)/bentonite	22.5	7.2–9.8	0.24 ± 0.05	7.95 ± 0.9
3	KF(20%)/bentonite	20.5	7.2–9.8	0.44 ± 0.05	35.5 ± 1.3
4	KF(30%)/bentonite	21.4	7.2–9.8	0.45 ± 0.05	64.5 ± 1.7
5	KF(40%)/bentonite	18.7	9.8–15.0	2.28 ± 0.05	98.2 ± 1.4
6	KOH(40%)/bentonite	17.3	9.8–15.0	2.12 ± 0.05	95.2 ± 1.2
7	K_2CO_3(40%)/bentonite	16.1	9.8–15.0	2.10 ± 0.05	95.0 ± 1.4

[a] Reaction conditions: molar methanol/oil: 6/1, temperature: 338 K, reaction time: 7 h, catalyst amount: 3 wt.%, calcination temperature and time: 773 K and 3 h.

the conversions obtained with KOH and K_2CO_3 at 40%. The yield of methyl ester increases significantly with increasing KF loading, and reaches $98.2 \pm 1.4\%$ at 40% by weight of KF as shown in Table 1. There appears to be a critical KF coverage below which there is little contribution of the KF, i.e., the methyl ester yields for the calcium bentonite particles with 0 and 10% KF by weight are similar. The methyl ester yield increases significantly between 10 to 40% KF. The relationship between the biodiesel yield and the KF content is linear in the 10–40% by weight of KF range (the correlation coefficient for linear regression, R^2, is > 0.99). The observed biodiesel yield of $98.2 \pm 1.4\%$ satisfies the biodiesel purity requirements of the European EN standard (EN-14103) which dictates that the purity of biodiesel should be at least 96.5 percent [38]. Since the European EN standard for biodiesel products could be comfortably met at the 40% KF level additional experiments were not carried out at other concentrations of KOH or K_2CO_3.

One major factor to consider is the increase of the basicity with increasing KF content. Basicity was shown to play a significant role on catalytic activity in comparison to surface area [33]. The increase in the biodiesel conversion is most pronounced at 40% by weight of KF at which the basicity is significantly greater than the basicity values at lower KF concentrations. The increase of the biodiesel yield with increasing basicity of the catalyst was noted in our previous studies on other types of catalyst supports for the transesterification reaction [22,24] and by Xie et al. [19,36]. Other factors of interest for the biodiesel yield are the formation of new K_2O at the catalyst surface and the leaching out of some of the K away from the surface of the catalyst particles during the process. These factors will be discussed later.

Are the values of the principle parameters of the transesterification reaction used for generating the results reported in Table 1 (6:1 molar ratio of methanol over canola oil, 7 h of reaction time, a reaction temperature of 338 K, and 3 wt.% of catalyst loading) optimum? For such heterogeneously catalyzed transesterification systems, the molar ratios of alcohol/oil were varied between 5:1 and 275:1 and the effects of the alcohol/oil ratio on rate of reaction were studied [10,19–22,24,35,36,40–44]. The stoichiometric molar ratio of methanol to canola oil is 3:1 for the transesterification reaction. An excess of alcohol (typically alcohol/oil > 6) is generally used to increase the yield of methyl esters and to facilitate glycerin separation. To investigate the effects of the alcohol to oil ratio for our bentonite catalyst supports the transesterification experiments were conducted by systematically changing the molar ratio of alcohol to oil, i.e., between from 6:1 to 18:1, while keeping
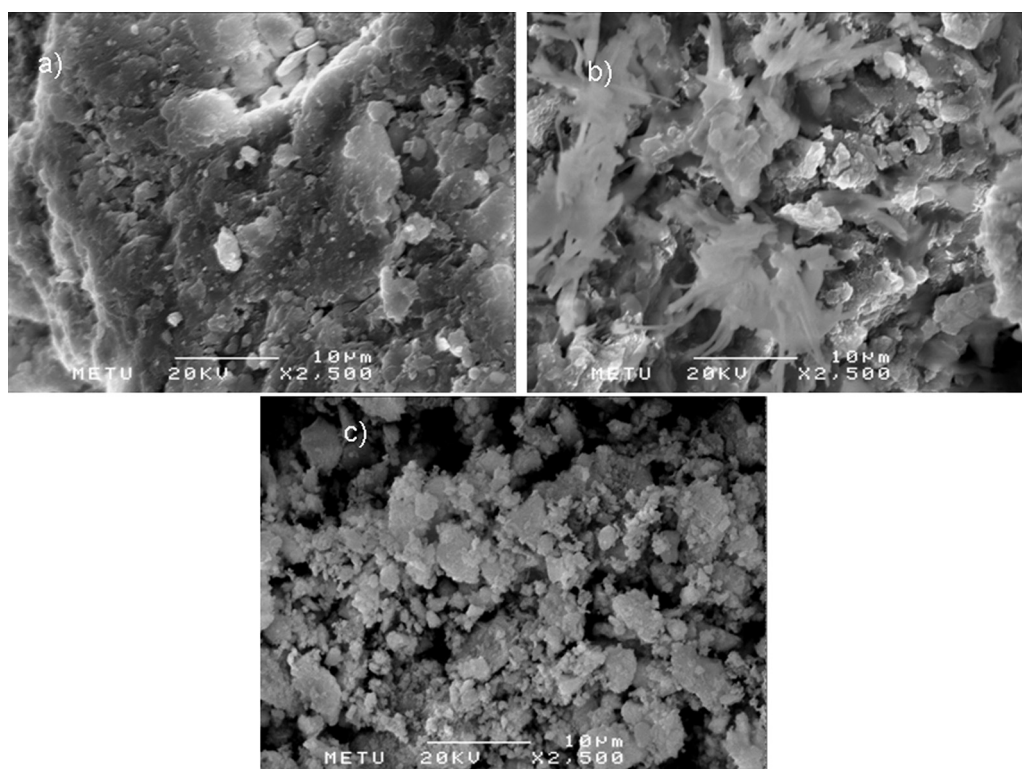
Fig. 3. SEM photographs of: (a) pure bentonite; (b) KF(40%)/bentonite (before transesterification, fresh catalyst); (c) KF(40%)/bentonite upon the transesterification reaction.
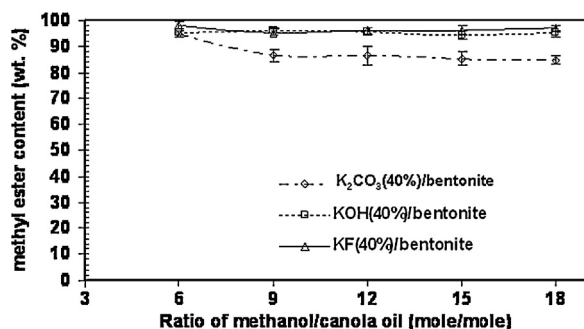
Fig. 4. Dependence of the methyl ester yield on the alcohol to oil molar ratio for three types of catalysts (T: 338 K, catalyst amount: 3 wt.%, reaction time: 7 h). The standard error range is ±0.86–3.64.

the temperature and the catalyst amount constant at 338 K and of 3 wt.%, respectively. KF(40%)/bentonite, KOH(40%)/bentonite and K_2CO_3(40%)/bentonite catalysts were used in these runs. The results are shown in Fig. 4 and suggest that altering the methanol/oil molar ratio in the 6–18 ratio range does not affect the methyl ester yield. These data, reported in terms of the 95% confidence intervals determined according to Student's-t distribution, confirmed that methanol/oil ratios that are greater than 6:1 do not increase the yield of methyl ester further. The highest methyl ester yield of 98.2 ± 1.4% could be reached at the molar alcohol/oil ratio of 6:1 for KF at 40%.

Reaction temperature can influence the reaction rate and the biodiesel yield because the intrinsic rate constants are strong functions of temperature. The effects of the reaction temperature on the yield of methyl ester were studied for [KF(40%)/bentonite, K_2CO_3(40%)/bentonite and KOH(40%)/bentonite] at four temperatures (298, 318, 333 and 338 K) while keeping the catalyst concentration constant at 3 wt.% and the methanol to oil ratio constant at 6/1. The maximum temperature studied i.e., 338 K, coincides with the boiling point of methanol. As shown in Fig. 5, the reaction rate was slow at low temperatures for the KF impregnated catalyst. The methyl ester yield was only 1.77% ± 0.77 after 7 h of reaction time at 298 K. The methyl ester yield increased with increasing reaction temperature and reached 98.2% ± 1.4 at 338 K. Considering that the rate changed little over the 318–338 K range, the suitable reaction temperatures for the transesterification of canola oil to biodiesel thus are in the 318–338 K range. It was also observed that the KOH supported catalyst is much more active at low temperatures in comparison to the KF and K_2CO_3 supported catalysts. This is an interesting effect and will be investigated in our future studies.

High activity of the synthesized catalysts can be achieved with strongly basic sites and a large surface area. The effects
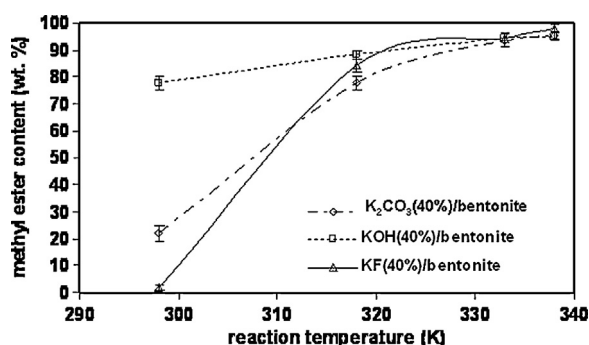

Fig. 5. Methyl ester yield versus reaction temperature for three types of catalysts (for methanol/oil ratio: 6/1, catalyst amount: 3 wt.%, reaction time: 7 h). The standard error range is ±0.77–2.99.
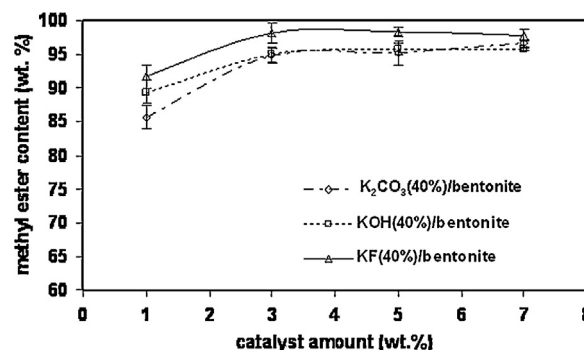

Fig. 6. Methyl ester yield versus the weight percent of the catalyst in the reaction mixture (for the methanol/oil molar ratio: 6/1, reaction temperature: 338 K, reaction time: 7 h). The standard error range is ±0.65–1.82.

of the catalyst concentration on methyl ester yield were investigated for KF(40%)/bentonite, K_2CO_3(40%)/bentonite and KOH(40%)/bentonite. The mass ratio of the synthesized catalyst to canola oil was varied within the range of 1.0–7.0% as shown in Fig. 6. The methyl ester yield increased with increasing catalyst amount and then reached a plateau value at a catalyst weight percent of about 3%. KF impregnated into bentonite catalyst generated a slightly greater methyl ester yield in comparison to the yields with KOH and K_2CO_3 impregnated catalysts. Consistent with our earlier discussion on the effect of basicity on biodiesel yield, the order of catalytic activities of the three types of K-functionalized catalysts was in line with their relative basicity, i.e., basicity of KF > KOH > K_2CO_3 as shown in Table 1. Similar conclusions were also reached in the 2006 study of Xie and Huang [35] when K salts were loaded to ZnO, to increase the basicity of the ZnO surfaces. The order of the catalytic activity was: KF/ZnO > KOH/ZnO > K_2CO_3/ZnO with the catalytic activity again in line with the relative basicity values of the catalysts.

3.3. Recovery and reuse of the catalyst

The recovery and reuse of the catalyst is an important factor in shaping of the economics of the use of the heterogeneous catalysis process for biodiesel manufacture. Reusability of the KF(40%)/bentonite catalyst was tested by consecutively recovering and then reusing the catalyst particles up to five times in conjunction with seven hour reaction cycles in the batch reactor (Fig. 7). For the reusability analysis the transesterification reaction of oil with methanol was carried out repeatedly under one constant set of operating conditions (methanol/oil: 6/1, catalyst amount: 3 wt.%, temperature: 338 K, reaction time: 7 h). Upon the completion of the transesterification reaction the catalyst particles were filtered out, recovered, washed with methanol several times, re-calcined at 773 K for 3 h and then reused as the catalyst of the next run. A fresh reaction mixture of methanol and canola oil was used at each cycle of the stability tests. The typical results of methyl ester yield with reaction time as a function of the number of recycling cycles are shown in Fig. 7. For all samples the rate of reaction is very high within the first hour (with the methyl ester yield reaching 80%).

The yield of methyl ester reaches 98.2 ± 1.4% (first use), 95.1 ± 1.2% (second use) and 93.4 ± 1.5% (third use) at the end of 7 h of reaction time. No significant differences of conversion were observed for the third (93.4 ± 1.5%), fourth (93.3 ± 1.3%) and fifth 93.3 ± 1.3% runs suggesting that the catalyst particles were stable. The observed modest reductions in the biodiesel yield upon recycle and reuse of the catalyst particles point to a reduction in catalyst activity. The decrease of the methyl ester yield from 98.2 to 93.4% is likely associated with the leaching out of some
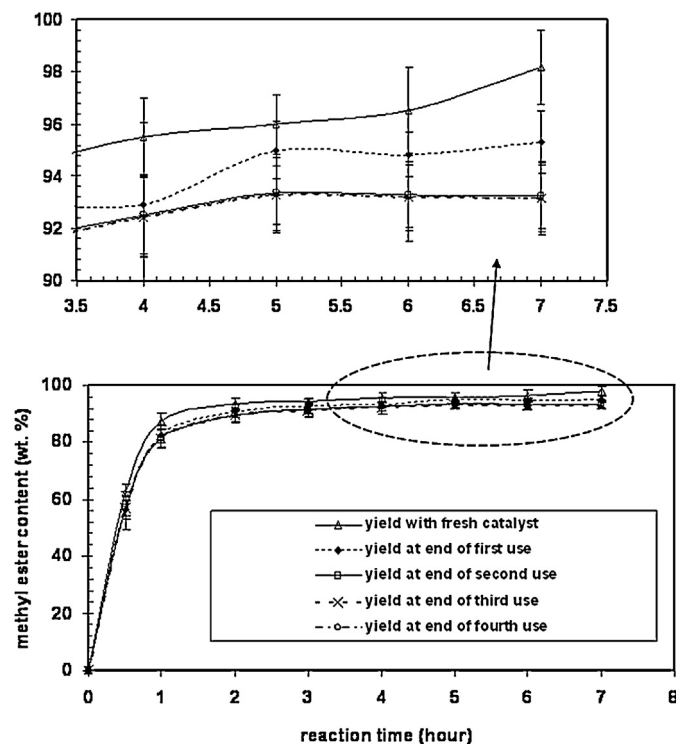
Fig. 7. The effects of recycling of the catalyst particles (KF(40%)/bentonite catalyst under molar methanol/oil: 6/1, temperature: 338 K, reaction time: 7 h, catalyst amount: 3 wt.%, calcination temperature and time: 773 K and 3 h). The standard error range is ±0.31–3.95.
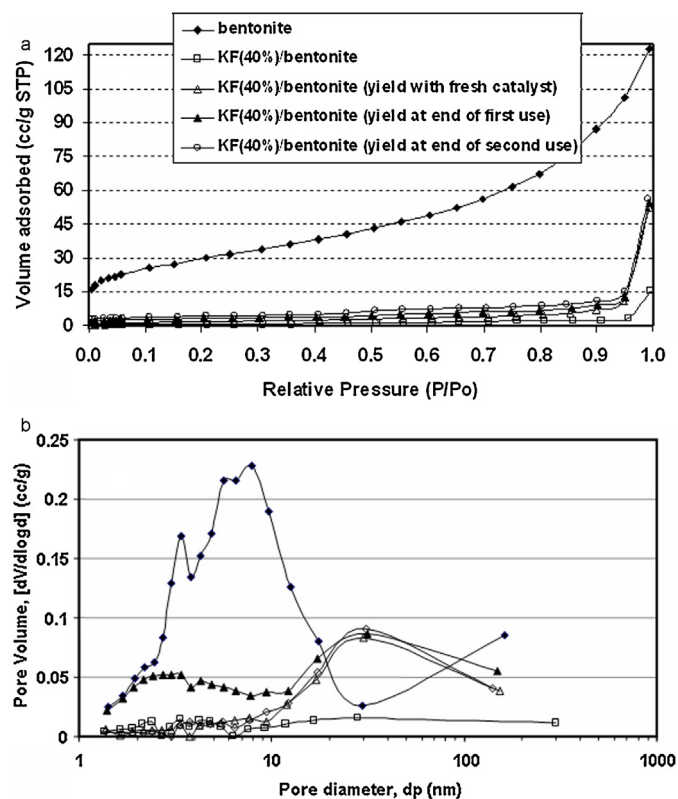

Fig. 8. (a) Nitrogen adsorption isotherms and (b) pore size distributions of calcium bentonite, KF(40%)/bentonite catalyst prior to transesterification reaction and KF(40%)/bentonite catalyst after transesterification reaction (first, second and third use).

of the K [24,31,33]. The relatively small 5% loss of activity that was observed at the end of third reuse of the KF(40%)/bentonite catalyst suggests that such leaching out of the K from our catalyst particles is not very significant. A similar conclusion is also reached from Fig. 8a and b which show that the surface area of the KF(40%)/bentonite catalyst did not deteriorate upon successive transesterification reactions. The average pore diameter appears to slightly increase after the first use of the KF(40%)/bentonite catalyst (Fig. 8b). However, no additional changes in pore volume were observed upon the subsequent reuses of the catalyst particles.

The catalyst particles collected after the first, second and third runs of the transesterification reaction were also characterized using XRD diffraction analysis (Fig. 9). The XRD patterns of calcium bentonite, KF and 40 wt.% potassium compounds-impregnated calcium bentonite catalysts [KF(40%)/bentonite] before and after transesterification reaction (successive three runs) are shown in Fig. 9. The XRD pattern of KF(40%)/bentonite catalyst was not significantly altered upon the transesterification reaction. This is consistent with the relatively low, i.e., only 5% loss of activity observed at the end of the third use of the KF(40%)/bentonite catalyst.

EDS analyses of the surfaces of bentonite, freshly prepared and recycled KF(40%)/bentonite catalyst particles are reported in Table 2. The sample surface was probed at three different locations with SEM-EDS. Each datum in Table 2 is the average value determined from three locations on the catalyst surface. The typical empirical formula for bentonite is (Al, Fe$_{0.67}$ Mg$_{0.33}$) Si$_4$O$_{10}$(OH)$_2$Na,Ca$_{0.33}$ [32]. As expected on the basis of this empirical formula, Al, Si, Ca, Mg, K, Ti and Fe are observed during EDS analysis. The K content of calcium bentonite is 4 wt.%. The K content of the surface of calcium bentonite impregnated with KF (40%) is 64.8 wt.%. This is a good indication that the KF loading

process into bentonite support material could indeed be carried out successfully. The recycled catalyst particles exhibit lower K contents in comparison to that of the fresh catalyst confirming that some of the K$_2$O which forms at the surface of the catalyst particles leaches out during the reaction, leading to the loss of activity and decrease of the methyl ester yield upon reuse.
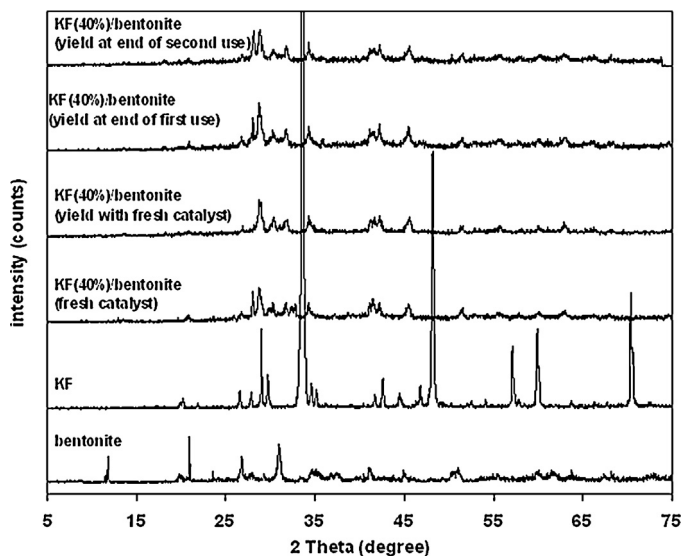

Fig. 9. XRD patterns of calcium bentonite, potassium fluoride and KF(40%)/bentonite catalysts before and after transesterification reaction (first, second and third use).

Table 2
EDS analysis of the surfaces of KF(40%)/bentonite catalyst particles prior to and after repeated transesterification reaction.

Weight (%)					
Element	Calcium bentonite	KF(40%)/bentonite (fresh)	KF(40%)/bentonite (1st use)	KF(40%)/bentonite (2nd use)	KF(40%)/bentonite (3rd use)
Mg	8.6	3.1	4.0	4.3	4.4
Al	10.5	2.7	4.2	4.1	4.1
Si	40.1	13.1	16.6	16.4	16.3
K	4.0	64.8	59.5	59.2	59.1
Ca	15.7	10.7	10.3	10.9	10.8
Ti	2.1	0.1	0.1	0.1	0.1
Fe	19.0	5.6	5.6	6.1	5.7

Reaction conditions: molar methanol/oil: 6/1, temperature: 338 K, reaction time: 7 h, catalyst amount: 3 wt.%, calcination temperature and time: 773 K and 3 h.

4. Conclusions

Catalysts consisting of calcium bentonite particles impregnated with aqueous solutions of three different potassium compounds (KF, KOH and K_2CO_3) and calcined at 773 K were tested for their activities in the transesterification reaction of canola oil with methanol for the synthesis of biodiesel. The transesterification parameters which were systematically varied were temperature (298–338 K), methanol/oil ratio (6:1–18:1), reaction time (1–7 h), and catalyst loading level (1-7 wt.%). KF generated a greater methyl ester yield in comparison to KOH and K_2CO_3, presumably due to the greater basicity of the catalyst surface when KF is utilized. A relatively high $98.2 \pm 1.4\%$ methyl ester yield could be obtained by using catalyst particles impregnated with 40% by weight of KF under the transesterification temperature of 338 K, catalyst loading concentration of 3 wt.%, molar methanol/oil ratio of 6 and 7 h of reaction time. This $98.2 \pm 1.4\%$ methyl ester yield satisfies the requirements of the European standard, EN-14103, which dictates that the purity of biodiesel should be at least 96.5 percent.

The stability of the KF impregnated catalyst supports was also investigated. The recycling and reuse of the catalyst particles up to three times gave rise to a modest decrease of their activity and led to a reduction of about 5% in their methyl ester yield. This decrease of activity is considered to be associated with the leaching out of the K_2O from the surface.

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